Evaluation of Dry Sorbent Technology for Pre-Combustion CO_2 Capture

(FE-0000465)

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URS Group

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2010 DOE/NETL CO_2 Capture Technology Meeting

Pittsburgh, PA • September 13-17, 2010

Project Objectives and Scope of Work

Objective

- Identify, develop, and optimize engineered sorbents for a dry sorbent process that combines CO_2 capture with the water gas-shift (WGS) reaction in syngas

Scope of Work

- Thermodynamic, molecular and process simulation modeling to identify/predict optimal sorbent properties and operating conditions
- Synthesis and characterization of SEWGS sorbents
- Experimental evaluation of sorbents for CO_2 adsorption and regeneration
- Techno-economic analysis

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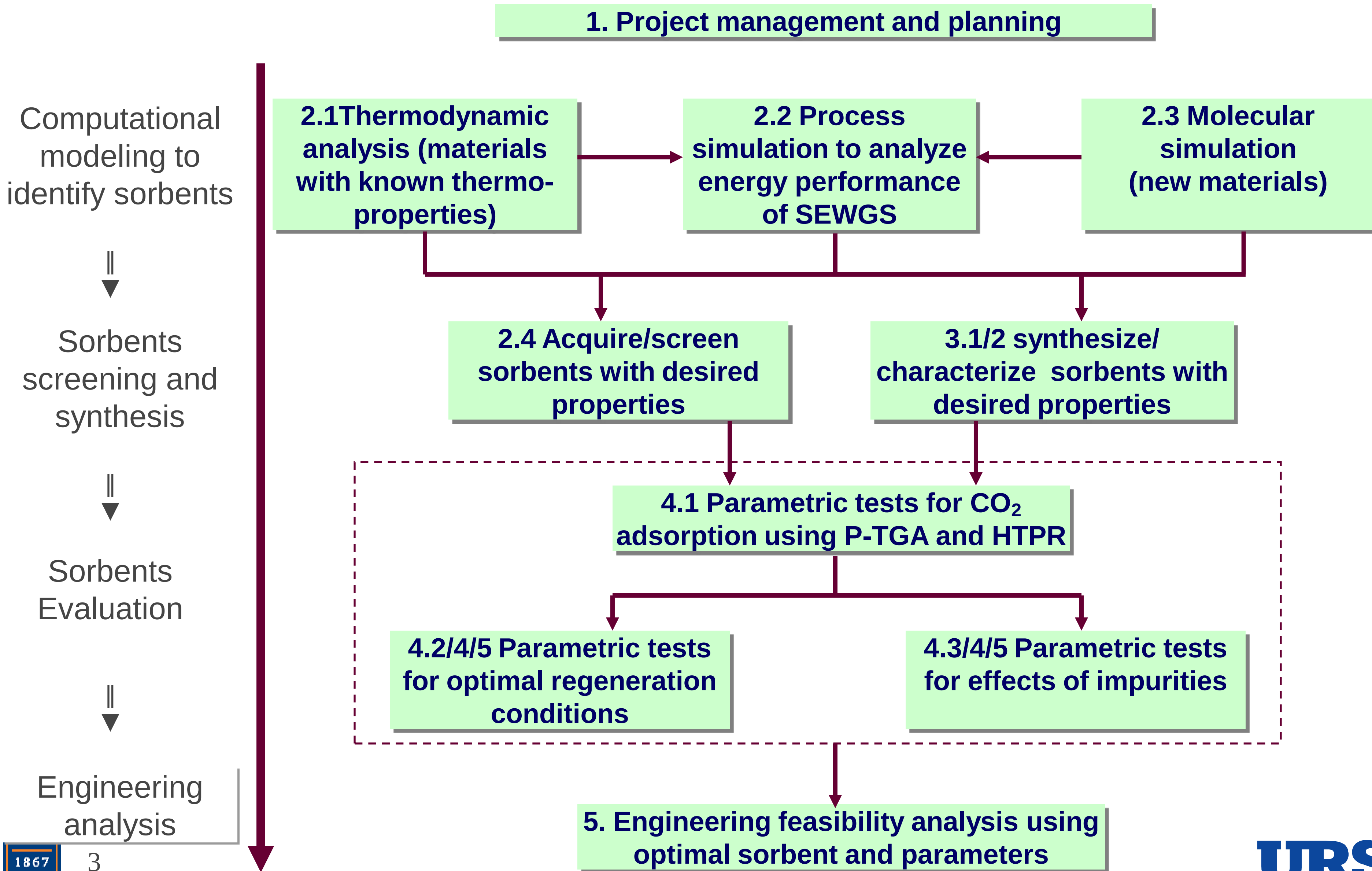
Research Tasks



Project Team

DOE-NETL:	**Susan Maley (COR)**	
ICCI:	**Joseph Hirsch (ICCI manager)**	
UIUC:	**Computation, sorbent synthesis/ screening**	
	Brandon Ito	**PhD candidate, Chemistry**
	Hong Lu	**Postdoctoral Research Associate**
	Yongqi Lu	**Research Chemical Engineer**
	Richard Masel	**Professor, Chemical & Bimolecular Eng**
	Massoud Rostam-Abadi	**Principal Chemical Engineer**
	Maryam Sayyah	**PhD candidate, CBM**
	Ken Suslick	**Professor, Chemistry**
URS Group:	**Prime Contractor; sorbent evaluation testing**	
	Carl Richardson	**Project Manager**
	William Steen	**Testing Manager**
	Jennifer Paradis	**Laboratory Director**

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Project Funding

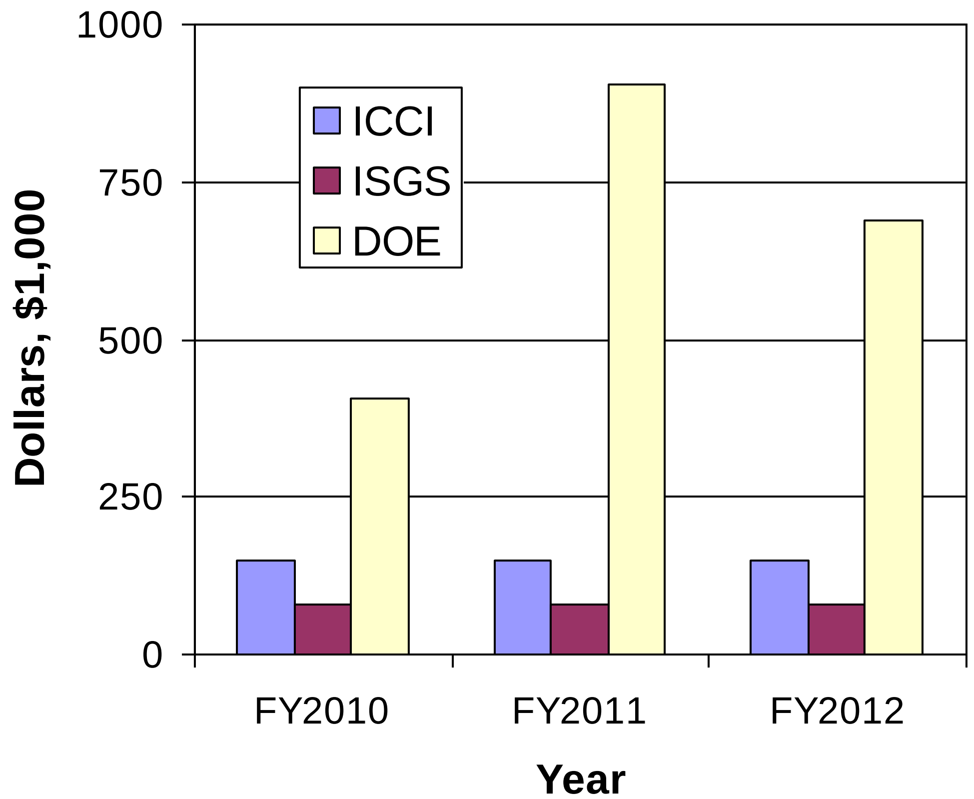
FY10: $ 633,669

FY11: $1,134,602

FY12: $ 916,123

Total: $2,684,394

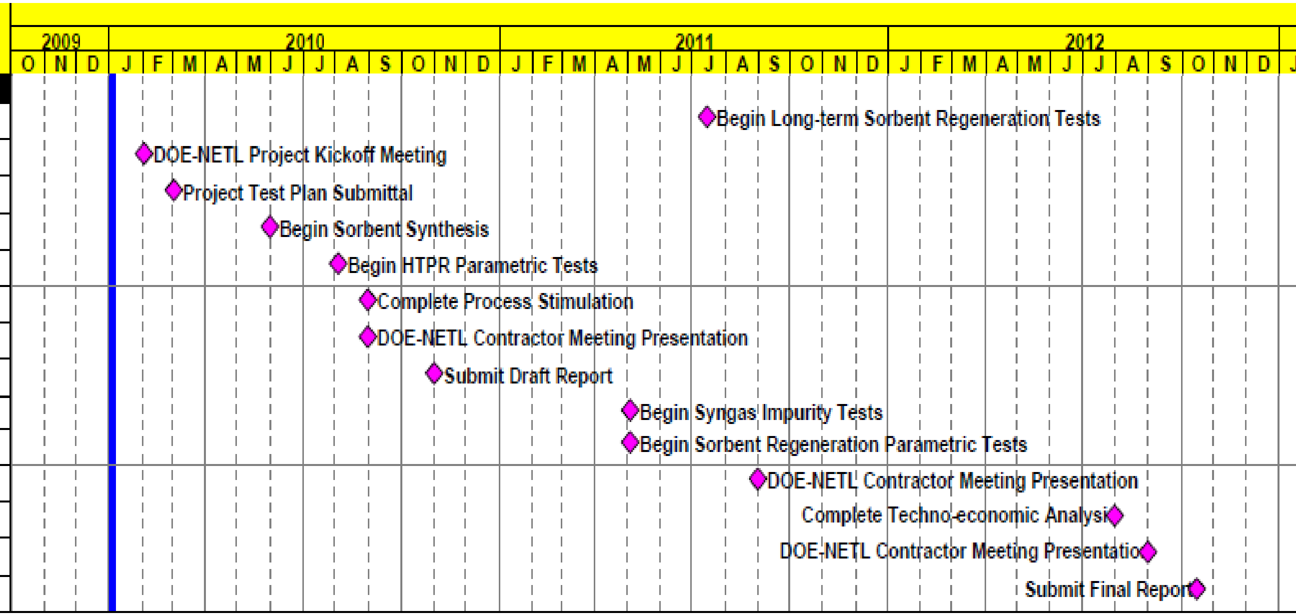
Where The Money is Coming From



Cost Share is 25%

Project Schedule

Activity ID	Activity Description
Milestones	
7.60	Begin Long-term Sorbent Regeneration Tests
7.15	DOE-NETL Project Kickoff Meeting
7.10	Project Test Plan Submittal
7.20	Begin Sorbent Synthesis
7.30	Begin HTPR Parametric Tests
7.25	Complete Process Stimulation
7.35	DOE-NETL Contractor Meeting Presentation
7.40	Submit Draft Report
7.45	Begin Syngas Impurity Tests
7.50	Begin Sorbent Regeneration Parametric Tests
7.55	DOE-NETL Contractor Meeting Presentation
7.65	Complete Techno-economic Analysis
7.70	DOE-NETL Contractor Meeting Presentation
7.75	Submit Final Report



Start Date 01OCT09

Early Bar

Progress Bar

Department of Energy

Sheet 1 of 1

DE-PS26-08NT00699-03

Period of Performance

Jan 1, 2010 to Dec 31, 2012

Technology Fundamentals/Background

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WGS vs. SEWGS in IGCC

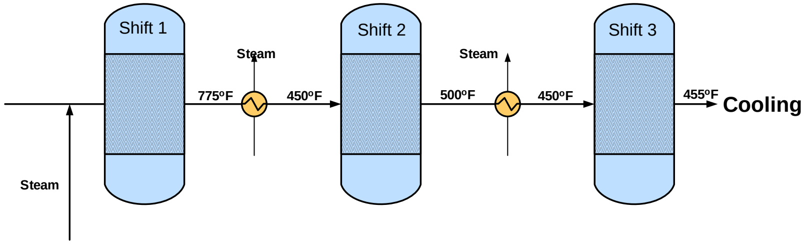
- Water gas shift (WGS) reaction

  $$CO + H_2O = CO_2 + H_2 \ (\Delta H = \text{-}41 \text{kJ/mol})$$

  – exothermic reaction, equilibrium (yield) favored at low temperatures (<300°C)

  – kinetics limited at low temperatures

  – multiple stages required



  ✓ CO conversion at 300–500°C (high-temp shift catalyst)

  ✓ Complete CO conversion at 180-300°C (low-temp shift catalyst)

- Sorption enhanced water gas shift (SEWGS)

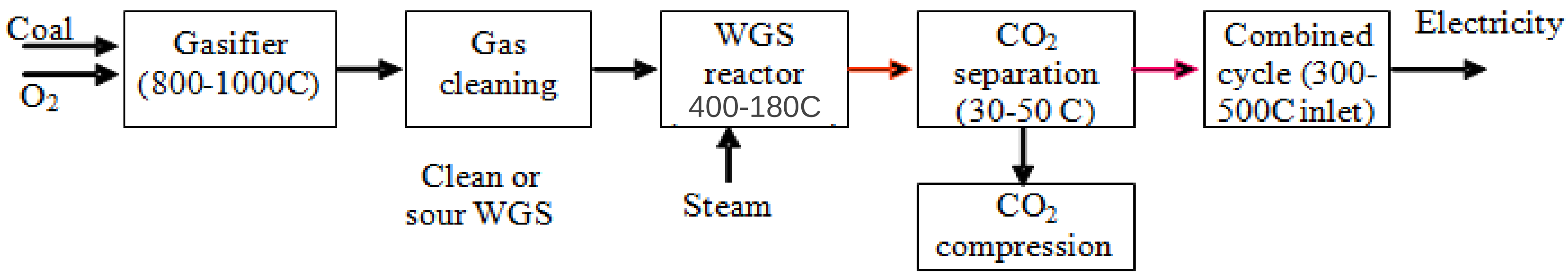
  $$CO + H_2O = CO_2 + H_2 \ (\varDelta H = \text{-}41 \ kJ/mol)$$

  $$\downarrow \ + \mathrm{Sorb} = \mathrm{Sorb} \cdot CO_2$$

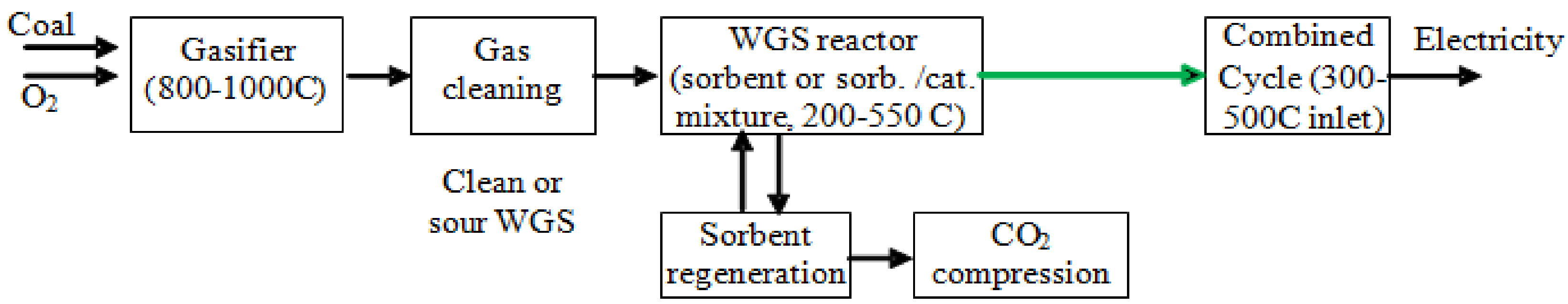
  – Simultaneous WGS + CO_2 Capture

  – Complete CO conversion at high temperatures (≥500 °C)

IGCC + SEWGS vs. Conventional IGCC



Conventional CO_2 capture



SEWGS

SEWGS

- ❑ No or limited WGS catalyst use
- ❑ No gas cooling/reheating
- ❑ No separate CO_2 capture unit required

Summary

- Project tasks performed as scheduled except MS (MS work delayed and expected to start in Oct. 2010)
- Suitable sorbents identified from thermodynamic and process analyses
- Sorbent synthesis initiated using three approaches
- A PTGA will be used for initial sorbent screening

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Progress and Current Status

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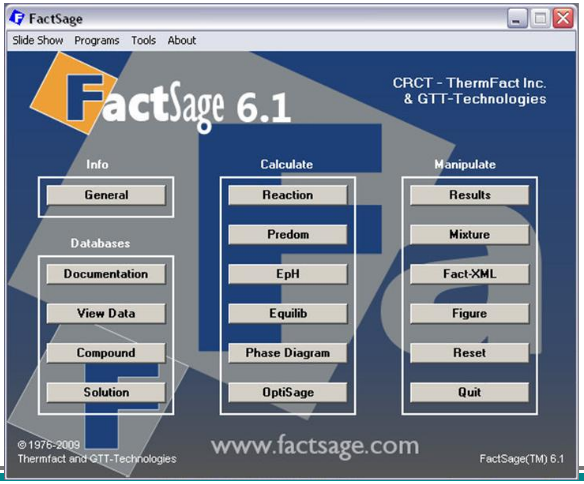
Task 2.1: Thermo Analysis

FactSage 6.1 software used in thermodynamic analysis

- Two modules for equilibria calculations
  - Reaction module
  - Equilib module (multi-reaction system)
- Two databases
  - Pure substances (4549)
  - Liquid and solid oxide or salt solutions (449)



Identification of SEWGS Sorbents

Initial screening thermo-analysis (40 sorbents)

40 metal oxides, zirconates, silicates, titanates (Li, Na, K, Cs, Mg, Ca, Sr, Ba, Y, Zr, Ni, Cr, Mo, Mn, Fe, Cu, Ag, Zn, Al, Si, Pb, Ce)

Adsorption at 200-600 °C in: (1) sorb+CO_2; (2) sorb+CO_2+H_2O; (3) sorb +CO_2 +H_2O+CO+H_2 ?

CO_2 adsorption/desorption equlibria (18 sorbents)

10 MeO (Mg, Mn, Sr, Cs, Ca, Li, Pb, Na, K, Ba); 3 zirconates (Li, Ca, Ba); 3 silicates (Li, Ca, Ba); 2 titanates (Ca, Ba)

Decomposition pressure at 800 °C and > 0.1 bar?

CO conversion under equilibrium (12 sorbents)

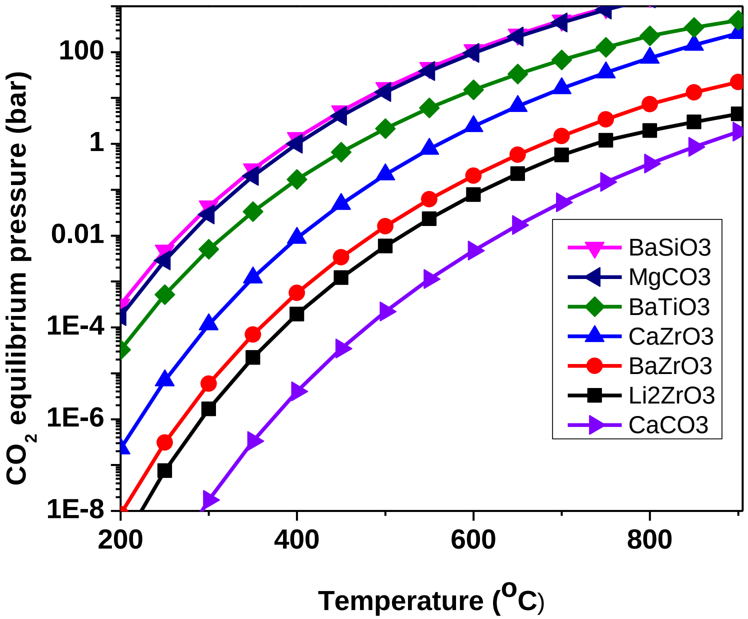
4 MeO (Mg, Mn, Ca, Pb), 3 zirconates (Li, Ca, Ba); 3 silicates (Li, Ca, Ba); 2 titanates (Ca,Ba)

High CO conversion at >400 °C ? (kinetics favored at high T)

2 MeO (Mg, Ca), 3 zirconates (Li, Ca, Ba); 1 silicate (Ba); 1 titanate (Ba)

Adsorption Equilibria of Selected Sorbents

CO_2 absorption



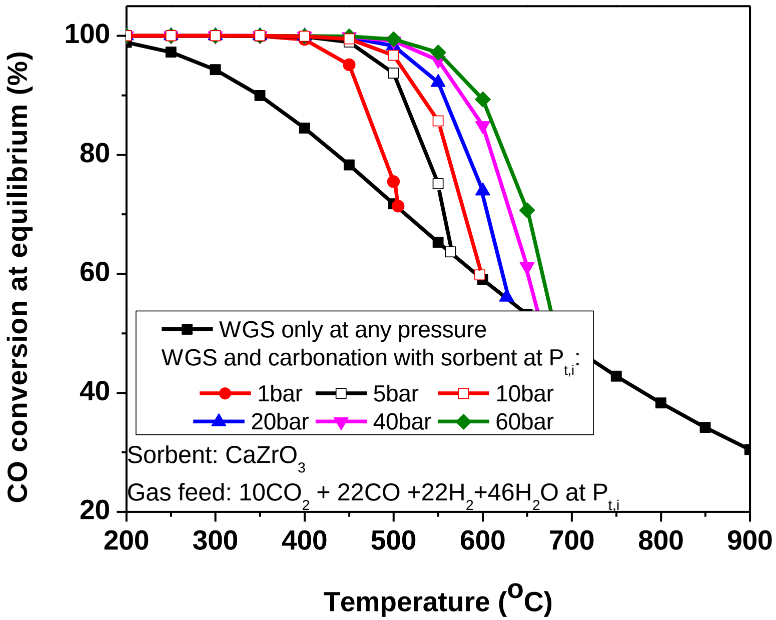
$MeO+CO_2 = MeCO_3$

$MeSiO_3+CO_2 = MeCO_3+SiO_2$

$MeTiO_3+CO_2 = MeCO_3+TiO_2$

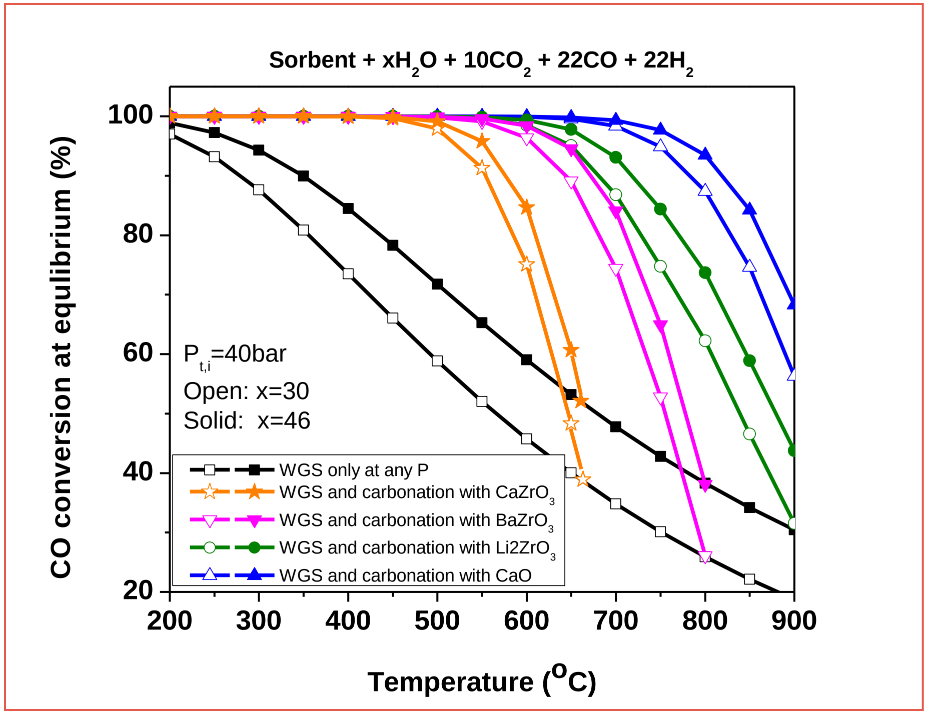
$MeZrO_3+CO_2 = MeCO_3+ZrO_2$

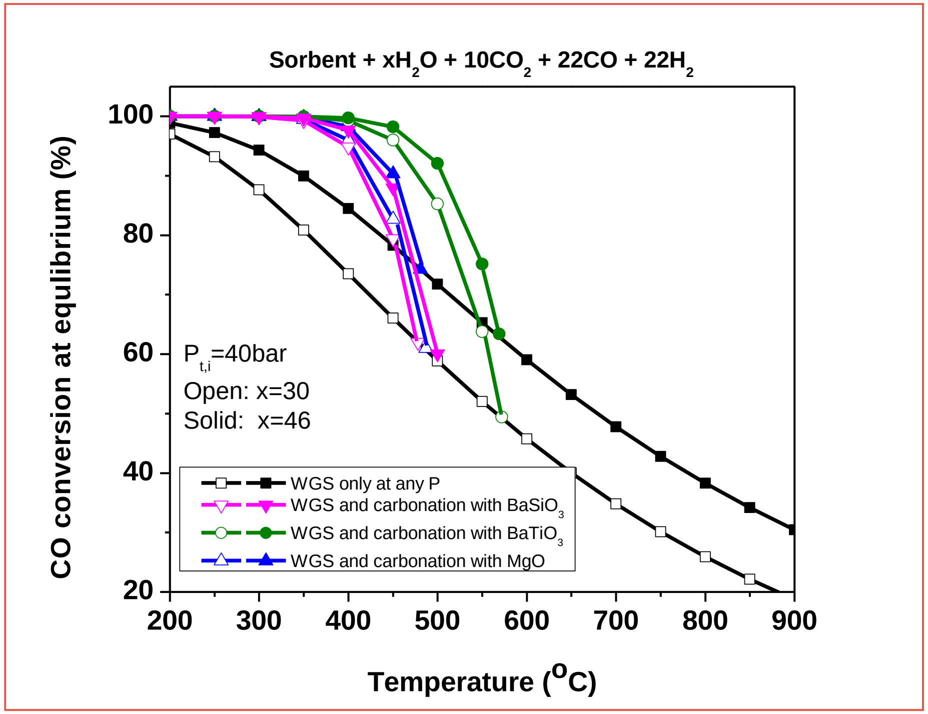
CO conversion



Initial gas composition:
10mol% CO_2, 22% CO, 22% H_2 and 46% H_2O

Water Vapor Pressure Impact on WGS Equilibrium





x=30: molar ratio of H_2O to CO of 1.4 (30:22)
x=46: molar ratio of H_2O to CO of 2.1 (46:22)

$$CO + H_2O = CO_2 + H_2 \ (\Delta H = -41 kJ/mol)$$

- Higher CO equilibrium conversion at the higher steam pressure
- Dependence of CO conv. on steam pressure in SEWGS less significant compared to WGS

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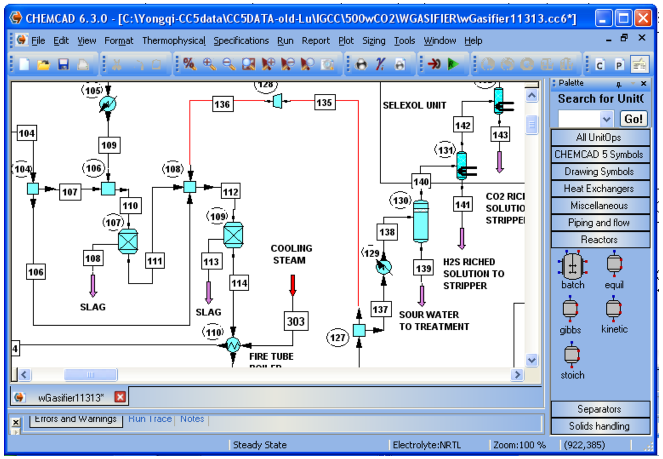
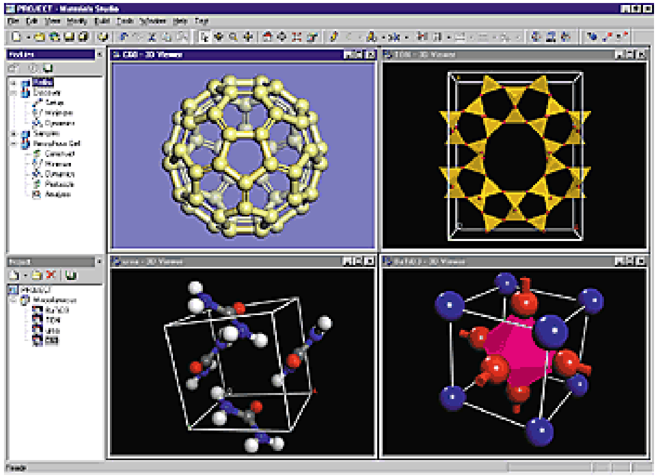
Task 2.2: Molecular Simulation, Process Simulation

- Process simulation of IGCC+SEWGS with selected sorbents
  - **Mass and energy balance calculation using CHEMCAD**
  - **Complete by 09/30/2010**

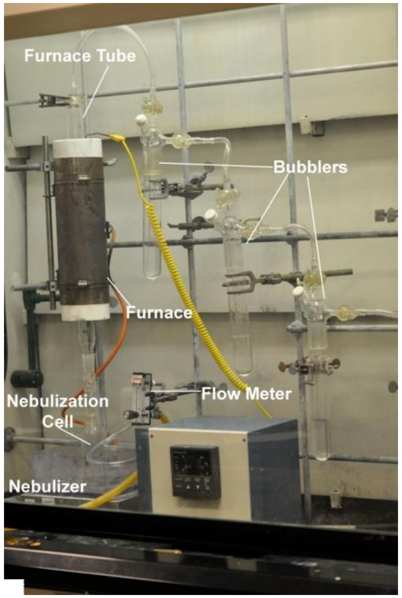


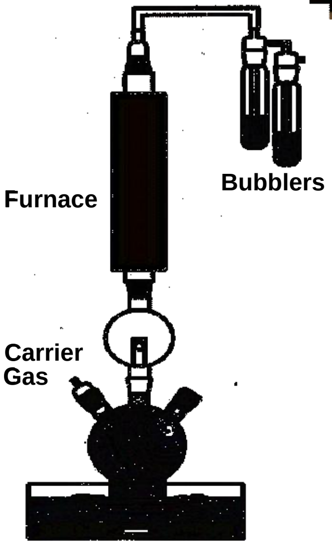
- Molecular simulation
  - **Start in 10/2010 (subcontract delayed)**
  - **Prediction of adsorption isotherms and thermodynamic properties**
  - **Prediction of reaction kinetics and dynamics of CO_2 adsorption**
  - **Initial MS of Ca, Mg compounds (aluminates, alumina silicates, silicates, zirconates)**
  - **Material Studio™ to be partly used**



Task 3: Sorbent Synthesis
Approach 1: Ultrasonic Spray Pyrolysis (USP)

- Dissolve sorbent precursor in solvents or water
- Precursor solution nebulized using high frequency ultrasound
- Carrier gas transports aerosol through the furnace
  - solvent evaporates
  - precursor decomposes to the product
- Product collected in bubblers and then isolated
- Easily scaled up





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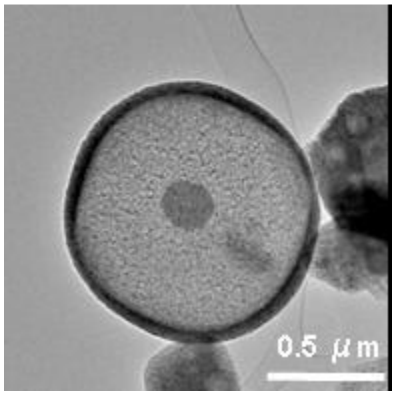
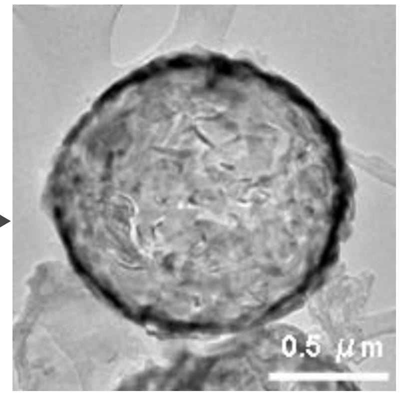
USP Products

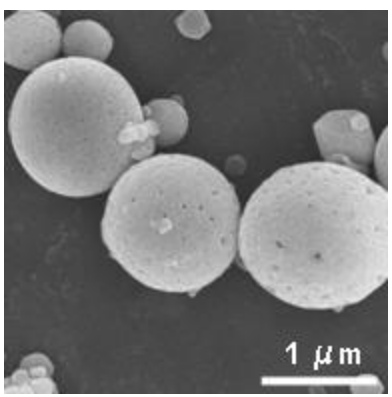
Images of USP product $CaCO_3$
Top: TEM
Bottom: SEM

Images of calcined product CaO
Top: TEM
Bottom: SEM

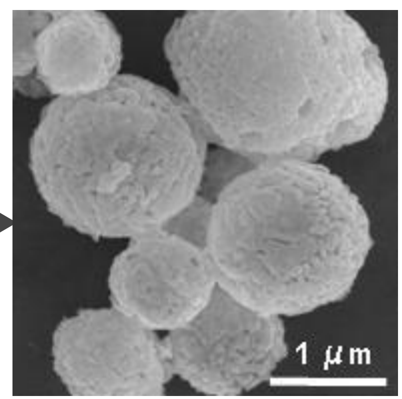


Calcine
600 °C





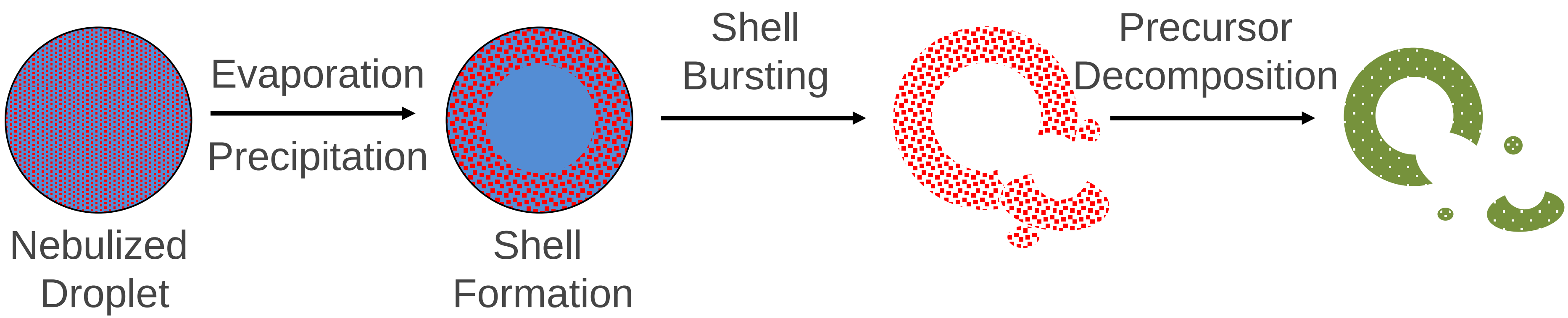
Calcine
600 °C



- Roughening of the particle surface is visible
- Grain size shrinks from 1332 Å to 393 Å upon calcination
- BET surface area (m^2/g)
  - USP: 40 - 75
  - CaO from precipitated $CaCO_3$: 9 - 36
  - Commercial lime:1-3

Predominately hollow spheres

Mechanism of Hollow Particle Formation in USP



- Nebulized droplets are carried through the furnace as isolated micron-reactors
- The temperature gradient in the droplet causes solvent evaporation and precursor precipitation on the outside of the droplet leading to shell formation
- As the rest of the solution evaporates, pressure from inside the shell causes it to burst, forming a large pore
- The precursor decomposes to the product and the shell becomes more dense

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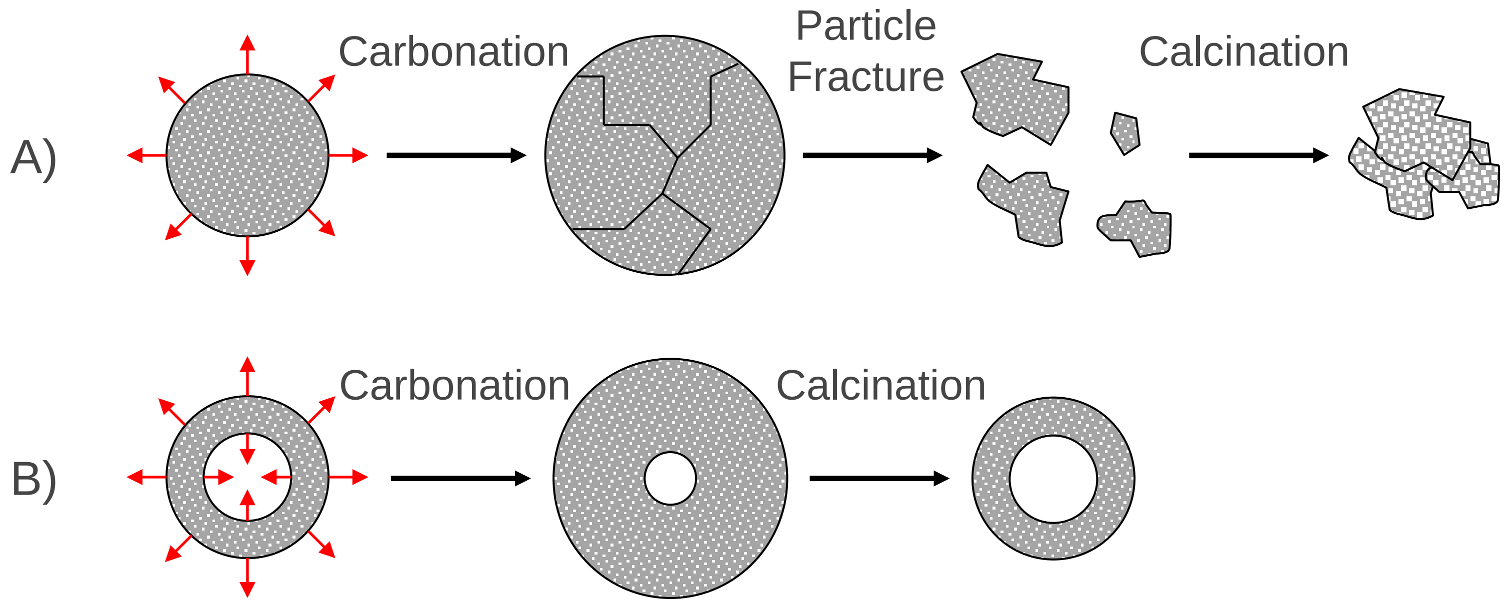
Advantage of Hollow Particles



$$CaO + CO_2 \rightleftharpoons CaCO_3$$

- 2.2 times volume expansion from CaO to $CaCO_3$[1]
- Solid CaO particles (*mechanism A*)
  - particle fracture increases the rate of sintering and loss of porosity[2]
- Hollow CaO particles (*mechanism B*)
  - permits expansion both inward and outward

[1]Blamey, J. *et al. Energ. Fuel,* **2010**, 24, 46405-4616.
[2]Abanades, J.C. and Alvarez, D. *Energ. Fuel,* **2003**, 17, 308-315.

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Task 3: Sorbent Synthesis Approach 2: Mechanical Alloying (MA)

- Mix multiple sorbent components at an atomic level
  - Microstructure
  - Properties tuned by controlling composition
  - Size cutting to nano-scale
  - Narrow particle size distribution and uniform composition
  - Properties superior to physical mixing

Shaker ball mill, SPEX 8000M

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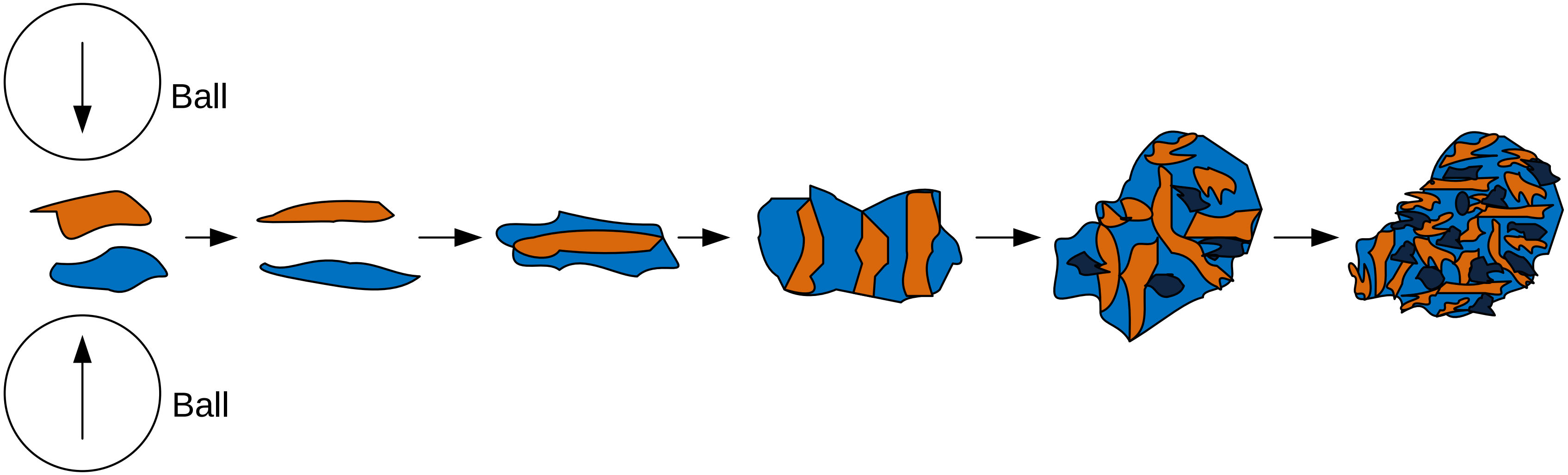
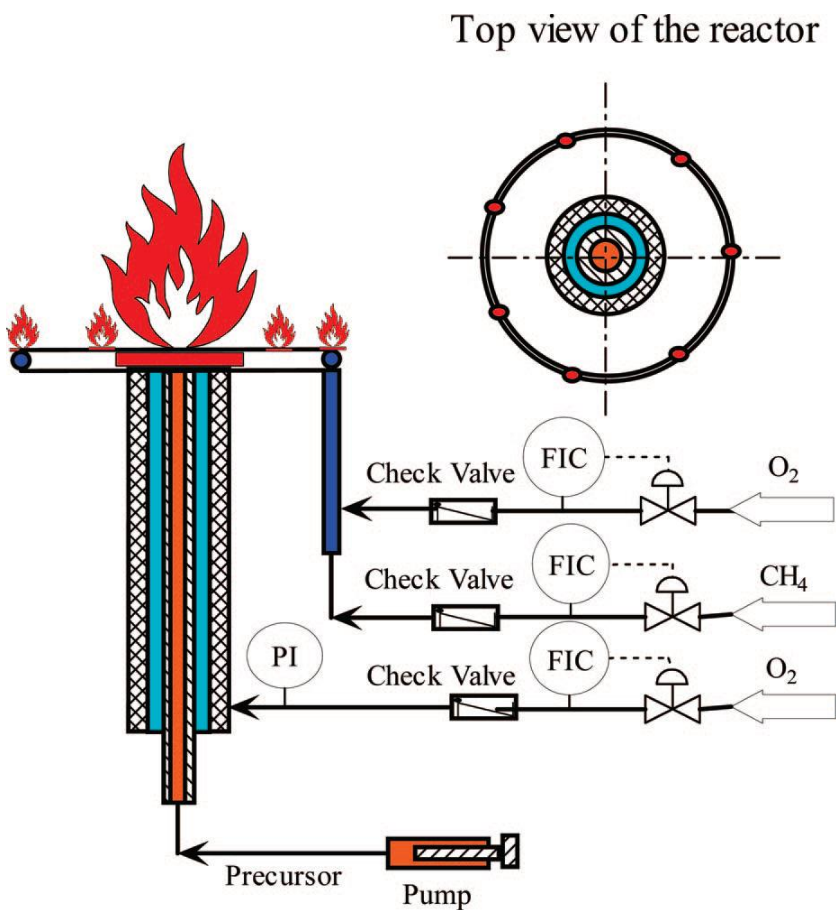
Mechanism of Mechanical Alloying

- Particles subjected to high energetic impact forces
- Particles flattened, fractured and welded
- Composite particles with layered structure formed



Task 3: Sorbent Synthesis
Approach 3: Flame Spray Pyrolysis (FSP)



- Combustible high heating value organic metal precursor
- Precursor solution atomized before burning/ pyrolysis
- Rapid heating and cooling during combustion/ pyrolysis produces sorbents with unique structure and morphology
- Properties tailored with selection of precursors and FSP conditions
- Good scalability and proven industrial applications

Task 4: Sorbent Evaluation Tests for CO_2 Adsorption

- High temperature & pressure reactor (HTPR)
  - Double shell reactor
  - Maximum 300 psig and 950 °C
  - 1’’ by 30’’ reactor tube
- PTGA (Cahn Thermax 500)
  - High T/P (1000 psi at 1000 C)
  - More efficient and accurate to operate than HTPR
  - Sorbent screening tests
- Characterization
  - XRD, BET, SEM, TEM

Future Testing

- Complete sorbent engineering analysis
  - Molecular simulation analysis
- Sorbent preparation activities
- Sorbent evaluation testing
  - PTGA and HTRP sorbent screening testing
  - Syngas simulation tests
  - Regeneration tests
- Engineering feasibility study

Acknowledgments

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